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A New Route to the Ni(O) 'Cradle' Complex $Ni_2(\mu\text{-}CO)(CO)_2(PPh_2CH_2PPh_2)_2$: μ-CO Ligand and Metal-centered Reactivity

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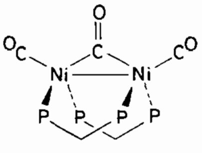
We report a new synthesis of the complex $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ (1) (dppm = bis(diphenylphosphino(methane)) and present evidence for both metal-centered and μ-carbonyl oxygen atom reactivity. The first binuclear nickel carbonyl derivatives of the type $Ni_2(CO)_3(P^\frown P)_2$, where $P^\frown P$ is a diphosphine ligand, were synthesized in 1966 [1]. Since then, several diphosphine ligands have been reported to form complexes of this general class [2, 3]. Osborn *et al.* [4] reported the surprising formation of the diphosphine complex 1 by the decomposition of the tripod phosphine complex $Ni(CO)_2(HC(PPh_2)_3)$.



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We reported that 1 is also formed by the reaction of the corresponding isocyanide complex $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ with CO_2 in the liquid phase [5] or photochemically with CO_2 in the gas phase [6]. We report herein a straightforward and convenient synthesis of 1 which follows eqn. (1).

$$2Ni(COD)_2 + 2dppm + 3CO \xrightarrow[\text{toluene}]{} Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2 + 4COD \qquad (1)$$

The reversible formation of a μ-CO adduct of 1 with AlR_3 (R = Me, Et) is also described. In the case of reaction of 1 with Brönsted acids, the Ni atoms are found to react in preference to the μ-CO ligand to form a μ-hydride di-nickel complex.

Experimental

All manipulations were performed under a N_2 atmosphere using Schlenk techniques. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrophotometer. ^1H and ^{31}P NMR chemical shifts were referenced to TMS and 85% H_3PO_4 respectively.

Freshly prepared $Ni(COD)_2$ [7, 8] (COD = 1,5-cyclooctadiene) was dissolved in THF to which 1 eq dppm was then added. The mixture was stirred for 15 min and the color changed from yellow to yellow–orange. CO gas (1.5 eq) was then added by syringe. The mixture was stirred for 30 min and stored at –20 °C overnight. The reaction volatiles were collected in a liquid N_2 cooled trap between the reaction flask and vacuum line. Any $Ni(CO)_4$ was disposed of by treatment of the trap distillate with bromine water. The remaining yellow solid was filtered, washed with ether, and dried under vacuum to obtain 1 in 89% yield.

$Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ (1)

Complex 1 was characterized by FT-IR, ^1H and $^{31}P\{^1H\}$ NMR. IR (KBr): ν(CO) 1970, 1948 and 1781 cm^{-1}. ^1H NMR (CD_2Cl_2): 2.61(m, 2H), 3.42(m, 2H), 6.92–7.38(m, 40H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2):δ 22.93(s). These data are in excellent agreement with previously reported values [4, 5]. The X-ray structure of 1 was recently reported [4].

$Ni_2(\mu\text{-}CO)(AlMe_3)(CO)_2(dppm)_2$ (2)

Complex 2 was prepared by addition of $AlMe_3$ to a toluene solution of 1 and was characterized by FT-IR and $^{31}P\{^1H\}$ NMR. IR (toluene): ν(CO) = 1998, 1981 and 1646 cm^{-1}. $^{31}P\{^1H\}$ NMR (toluene): δ 24.09(s).

$[Ni_2(\mu\text{-}CO)(\mu\text{-}H)(CO)_2(dppm)_2][PF_6]$ (3)

Complex 3 was prepared as a bright yellow crystalline solid by addition of HPF_6 to a toluene solution of 1, and was characterized by FT-IR, ^1H and $^{31}P\{^1H\}$ NMR. IR (KBr): ν(CO) = 2041 and 1867 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.1–8.0(m, 40H), 3.12(m, 2H), 3.3(m, 2H) and –11.0(p, 1H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 31.34(s). *Anal.* Calc. for $C_{53}H_{45}O_3P_5Ni_2F_6$. C, 56.98; H, 4.03. Found: C, 56.50; H, 4.10%.

Results and Discussion

The reaction of $Ni(COD)_2$ with dppm and CO in toluene represents a convenient synthesis of complex 1. Yields approach 90% and the preparation does not require directly handling of $Ni(CO)_4$ or the use of hydridic reducing agents [9].

As part of our studies, we have surveyed the reactivity of 1 with Lewis and Brönsted acids. In earlier studies, we found that the μ-isocyanide ligand of the complex $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$

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possesses unusually high N-atom Lewis basicity, and readily undergoes N-protonation or N-alkylation [10]. The μ-CO ligand of **1**, however, behaves only as a weak base. The reaction of **1** with excess AlR_3 (R = Me, Et) in toluene leads to the appearance of ν(CO) bands at 1998, 1981 and 1646 cm^{-1}. The pure adduct $Ni_2(\mu\text{-}CO(AlMe_3))(CO)_2(dppm)_2$ [1] can be prepared by removal under vacuum of toluene solvent and excess $AlMe_3$. The low frequency bridging ν(CO) band of **2** suggests the complex exists as a μ-$CO(AlMe)_3$ adduct. Similar adducts of Fe and Ru carbonyl clusters have been reported by Shriver [11, 12]. Complexes **1** and **2** exist in equilibrium in toluene solution (eqn. (2)).

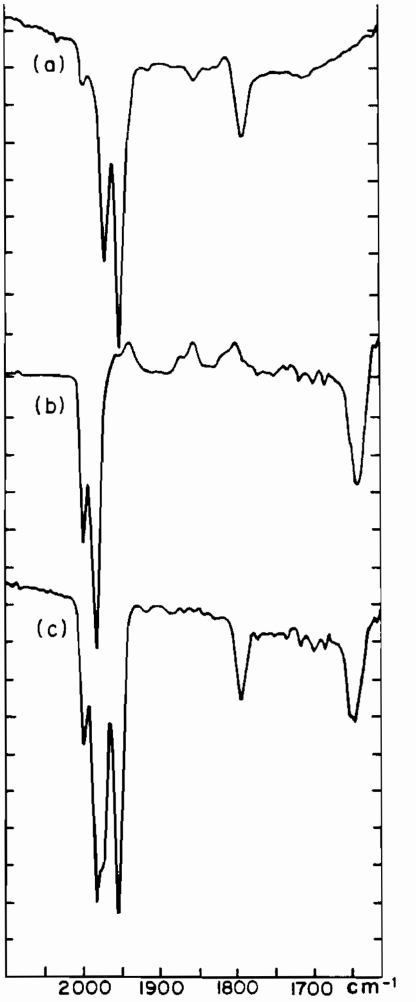
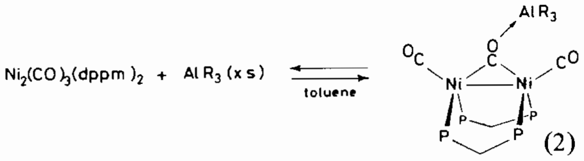


Fig. 1. FT-IR spectra in the ν(CO) region showing (a) $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ (**1**); (b) $Ni_2(\mu\text{-}CO(AlMe_3))(CO)_2(dppm)_2$ (**2**); and (c) an equilibrium mixture of **1** and **2** resulting from the dissolution of **2** in toluene.



1 **2**

R = Me, Et

Dissolution of pure **2** in toluene produces ν(CO) bands characteristic of both **1** and **2**. Figure 1 presents the FT-IR spectra in the ν(CO) region of (a) pure **1**, (b) pure **2**, and (c) an equilibrium mixture of **1** and **2** produced upon dissolution of **2** in toluene.

In contrast to the μ-CO O-atom basicity of **1** with respect to AlR_3 (R = Me, Et), reaction of **1** with protons leads to metal-centered reactivity. The reaction of **1** with HPF_6 in toluene leads to the complex $[Ni_2(\mu\text{-}CO)(\mu\text{-}H)(CO)_2(dppm)_2][PF_6]$ (**3**). Complex **3** has been characterized by IR, ^1H and $^{31}P\{^1H\}$ NMR and elemental analysis. A high frequency bridging or semibridging ν(CO) band is evident at 1867 cm^{-1}. The ^1H NMR reveals a single hydride resonance, centered at −11.0 ppm and symmetrically coupled to all four phosphorus nuclei (J_{P-H} = 27 Hz). The hydride ^1H NMR spectrum and proposed structure of **3** are presented in Fig. 2.

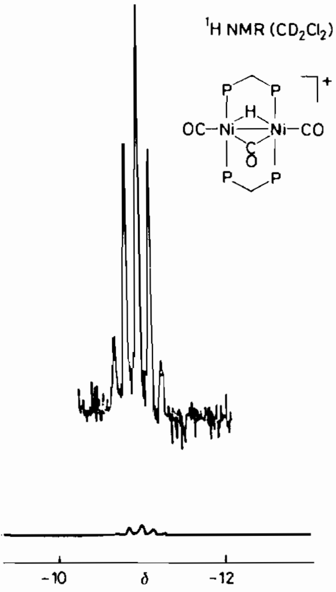


Fig. 2. ^1H NMR of $[Ni_2(\mu\text{-}CO)(\mu\text{-}H)(CO)_2(dppm)_2][PF_6]$ (**3**) in the hydride region.

In summary, a convenient synthesis of **1** from $Ni(COD)_2$, dppm and CO has been developed. Complex **1** exhibits both μ-CO-centered and metal-centered reactivity with AlR_3 (R = Me, Et) and HPF_6 respectively.

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